TEKNILLINEN TIEDEKUNTA

XRD-based clay mineralogy of the Landsort Deep Sediments, Baltic Sea (IODP, Site M0063)

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ABSTRACT

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Abstract

The Baltic Sea is an intracontinental basin and its deepest deep is Landsort Deep (459m). The IODP Expedition 347 was able to recover about 115 meters in depth of undisturbed sediment deposits from the deep. These clay minerals and other sediments are the record of Holocene, more precisely the time after the last glaciation. Analysing illite, kaolinite, chlorite and smectite groups clay minerals with x-ray diffraction (XRD) method, can the Baltic Sea stages be studied. The aim of this thesis is to study the paleoenvironments of past Baltic Sea stages and possibly discover the provenance areas of clay minerals. Also, the possible anoxic events of the Baltic Sea Basins bottom are of interest.

The clay mineral samples were made in Oulu Mining Schools facilities for the XRD-analysis that was done in Centre for Material Analysis, University of Oulu. After analysing it came to be clear that there were no smectite clay minerals in any of the samples. This finding coincided with some other studies done from sediment materials from different parts of the Baltic Sea Basin. Illite, chlorite and kaolinite group clay minerals percentual values changed throughout the different stratigraphic deposits. Previous studies lithostratigraphic divided the sediment record to different units and subunits and most of the samples studied in this thesis correlated to them. Some samples in this thesis could really be from other subunits and slightly change the lithostratigraphy. Kaolinite/chlorite ratio is a good indicator in discovering changes in the Baltic Seas stages. Excess kaolinite usually comes from rivers from areas that have Paleozoic-Mesozoic era rocks and paleosols, but in this thesis it is reasonable to assume that sometimes the North Sea is the source of kaolinite, sometimes even both. High chlorite percentage can be related to short transportation distances because chlorite minerals are weakly resistant to weathering and transportation. Of course, chlorite minerals can come as ice rafted debris (IRD). High percentage of illite minerals are a result of intense melting of glacier and when this melting happens closer to continent. The undisturbed stratigraphy with no evidence of bioturbation is a good indicator of anoxic events in basin bottom and this correlates to other studies that say that Landsort Deep has been anoxic most of the time the last 7000 years.

Most of this thesis study results are similar to other studies from the Baltic Sea and previous studies from the Landsort Deep. Only few samples did not correlate to previous assumptions of lithostratigraphy and are most likely from other units then assumed. XRD is generally a good reliable way to study clay minerals.

Additional Information

Keywords: IODP, Landsort Deep, clay minerals, XRD, The Baltic Sea, kaolinite/chlorite ratio

TIIVISTELMÄ

OPINNÄYTETYÖSTÄ Oulun yliopisto Teknillinen tiedekunta

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Tiivistelmä

Itämeri on mantereensisäinen allas ja sen syvin syvänne on Landsortin syvänne (459m). IODP:n tutkimusmatka 347 sai kairattua noin 115 metriä häiriintymätöntä sedimentti kerrostumaa syvänteestä. Nämä savisedimentit ja muut sedimentit ovat Holoseenin ajalta, tarkemmin sanottuna viimeisimmän jääkauden jälkeistä aikaa. Illiitti, kaoliniitti, kloriitti ja smektiitti ryhmiin kuuluvia savimineraaleja analysoidaan x-ray diffraktio (XRD) metodilla ja näiden savimineraalien avulla voidaan tutkia Itämeren vaiheita. Tämän pro-gradun tarkoituksena on tutkia Itämeren paleoympäristöjä, selvittää savimineraalien lähtöalueita ja tutkia mahdollisia Itämeren pohjan hapettomia olosuhteita.

Savimineraalinäytteet tehtiin Oulun kaivannaisalan yksikön laboratoriossa ja XRD-analyysin suoritettiin Materiaalianalyysikeskuksessa Oulun yliopistolla. Analyyseistä selvisi, että näytteissä ei ollut ollenkaan smektiitti mineraaleja ja tämä menee yksiin joidenkin aikaisempien tutkimuksien kanssa Itämeren altaasta. Aikaisemmat tutkimukset luokittelivat sedimentti kerrostuman litostratigafisiin yksiköihin. Illiitti, kloriitti ja kaoliniitti ryhmien savimineraalien prosentuaaliset määrät vaihtelivat riippuen siitä, mistä yksiköstä on kyse. Suurimmalta osin pro-gradun näytteet menivät yhteen aikaisempien tutkimuksien litostratigrafioiden kanssa, mutta parin näytteen savimineraalien määrät viittasivat, että ne kuuluvat toiseen yksikköön kuin ne olivat ajateltu alun perin. Kaoliniitti/kloriitti suhdeluku on hyvä indikaattori Itämeren vaiheiden tutkimiseen. Suuri määrä kaoliniittia tulee yleensä joista jotka virtaavat paleo- ja mesotsoonisten kivien ja kerrostumien lävitse. Tämän pro-gradun tuloksien perusteella myös Pohjanmeri on kaoliniitin lähde alue, ja joissakin tapauksissa kaoliniittia tulee sekä mantereelta että Pohjanmereltä. Korkea kloriitti pitoisuus voidaan yhdistää lyhyihin kuljetusmatkoihin, koska kloriitti ei kestä hyvin rapautumista ja kuljetusta. Kloriitti voi tulla myös jäälauttojen mukana. Illiitin korkeat pitoisuudet liittyvät myös jäätikön sulamiseen ja eritoten mantereisella alueella. Landsortin syvänteen kerrostuman häiriintymättömyys ja se, ettei siinä ole juurikaan jälkiä bioturbaatiosta, voidaan Landsortin syvänteen olleen hapeton. Muissakin tutkimuksissa todettiin, että Landsortin syvänne on ollut pääsin osin hapeton viimeiset 7000 vuotta.

Pääosin tämän pro-gradun tutkimuksien tulokset olivat samansuuntaisia kuin muissa Itämerestä tehdyissä tutkimuksissa. Van muutama näyte ei korreloitunut samoin kuin aikaisemmat oletukset litostratigrafiasta. XRD on yleisesti ottaen hyvä tapa tutkia savimineraaleja.

Muita tietoja

Avainsanat: IODP, Landsort Deep, savimineraalit, XRD, Itämeri, kaoliniitti/kloriitti suhdeluku

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1. INTRODUCTION

In 2013 Integrated Ocean Drilling Program (IODP) Expedition 347 was made at the Baltic Sea. One of the drilling sites (Site M0063) was at Landsort Deep, the deepest deep (459m) in the Baltic Sea (Andrén *et al.* 2015a). The deep is situated north from the coastline of Stockholm (Fig. 1.1) and from this site, they were able to drill the sediments from water depth 437.1 m (Andrén *et al.* 2015b) all the way up to 115.81 meters below sea floor (mbsf). In this thesis clay minerals assemblages are studied from this site by using x-ray diffraction (XRD) method. The Baltic Sea is well studied and there are many articles regarding e.g., chemistry, stratigraphy and paleoenvironments of the Baltic Sea and its surrounding areas (e.g., Harff *et al.* 2011; Andrén *et al.* 2015a, b, c; Kelly & Passchier 2018).

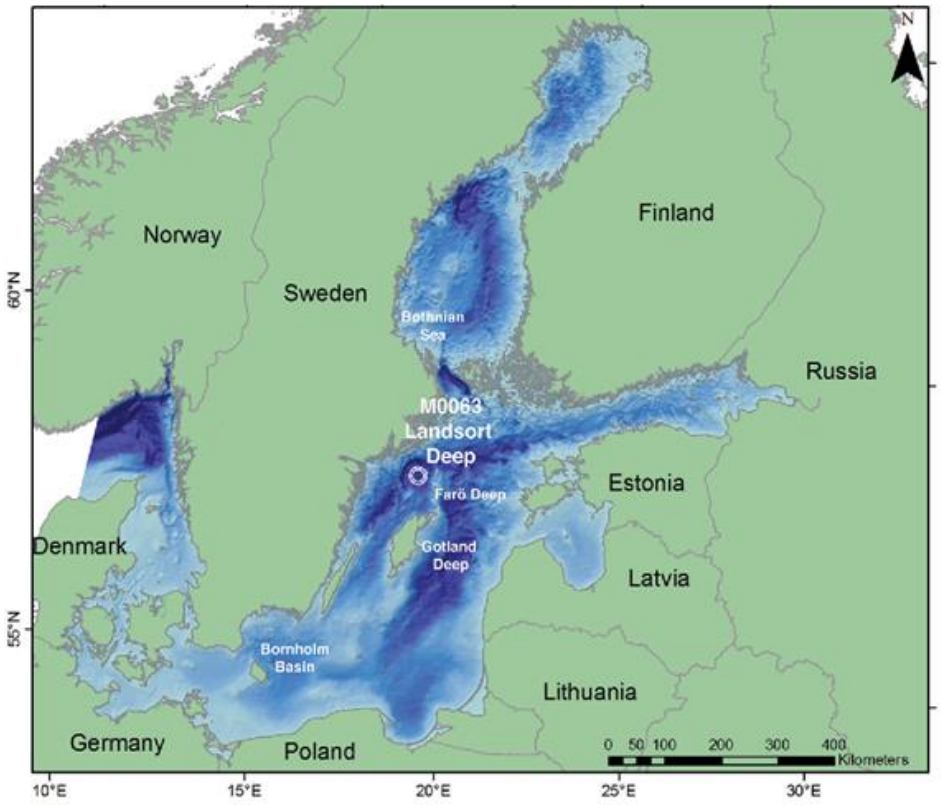

Figure 1.1 A map of the Baltic Sea. Site M0063 in Landsort Deep is almost in the middle of the sea. Landsort Deep is 459 meters deep and the frilling went up to 115.81 mbsf (meters below sea floor). Bathymetry of hte sea is marked as blue colour, darker the colour the deeper the sea. The figure is modified from Hardistry et al. (2016).

A specific aim of this study is to consider paleoenvironmental changes with the help of clay minerals and possibly detect indications of occasional anoxic conditions at the sediment-water interface of the Landsort Deep. Occurrence of detrital and authigenic minerals can help with understanding of the basin environment as well its drainage area. Detrital mineral assemblages can help to understand the provenance of the minerals and clay minerals in particular reveal those climate conditions in the source area during weathering and character of provided source materials and the mode of sediment transport and burial. Clay minerals can for example be used to reconstruct paleoclimates and/or deciphering sedimentary processes (Ehrmann *et al.* 1992).

The structure of this thesis is to start with the basics of clay minerals are, what clays are, how they are formed and what kind of environmental concerns are related for each clay mineral. After that, the focus is on Landsort Deep, the IODP expedition 347, the general geology of the area and evolution of the Baltic Sea. Then the identification method XRD is also discussed before materials, used methodological practise, results and discussion based on my own discoveries.

2. CLAYS AS MINERALS

Clays in sediments are fine-grained minerals that are less than 2μm in diameter and are mostly phyllosilicates. Clay minerals are almost always the result of exogenous processes for example like chemical weathering or thermal variations. Some clay minerals change their volume when there is water involved. This swelling property divides clays in to swelling and non-swelling (Velde 1992; Lewis & McConchie 1994). Clay particles can change their volume even by 95% (Velde 1995). Although clays are not the largest group of components when thinking of other minerals like olivine or feldspar (Meunier 2005), they certainly are the largest sediment group (Lewis & McConchie 1994; Aboudi Mata *et al.* 2017). Clay minerals are close to peoples everyday life, for example in cosmetics (Roselli *et al.* 2015), paper making (Miyamoto & Watanabe 1982) and environmental chemistry (Gu *et al.* 2019). Human activities also affect the processes of clay forming, for example increased weathering caused by farming. Clays can also be one of the reasons of environmental hazards like landslides (Meunier 2005). Some clay sediments that have been layered in marine- and brackish-water environment during late glacial and postglacial time are called quick clay. This type of sensitive sedimentation behaves like a liquid when salt has disappeared from it and the structure of the sediment layer is disturbed (Clague & Stead 2012). For example, quick clay sediments were the cause of the Gjerdrum landslide in Norway 2020.

The different processes and environmental conditions are evident in the clay's mineralogy, and they help interpret paleoenvironments (Velde 1992). Of course, caution should be used when interpretating the weathering or deposition environments because one type of clay mineral can be formed in a different environment where it is deposited, or the same environment can produce different types of clay minerals depending on controls like the source rock. When studying the stratigraphic column, changes in clay mineralogy can be a result of a minor change in the source areas tectonics, relief and/or drainage (Lewis & McConchie 1994).

Detrital minerals are the product of the parent rocks composition and the conditions of the environments during the time of weathering. Detrital minerals or clays are not produced in-situ, in other words at the sedimentary basins, like authigenic minerals are (Meunier 2005). If sedimentary conditions are relatively stable, isotopic composition of detrital material can be unchanged. Clay materials isotopic composition can stay unaltered during the transportation and even after being buried for several hundreds of meters.

This makes detrital clays valuable when determining the origin of sediments and when studying the conditions of the source areas (Meunier 2005).

Detrital minerals are a product of erosion but authigenic minerals are formed on site within deposited sediments when temperature rise is suitable due to burial. Authigenic minerals are formed physically and chemically, and these minerals can help to decipher the sediment conditions after deposition. Authigenic processes often lead to metamorphic processes but that needs more pressure, heat, and depth (Middleton 2003). Illites, smectites, kaolinites and chlorites can all have authigenic forms also. In shallower environments during burial diagenesis come clays can change from smectites to illite (Middleton 2003, Bruno 2009), or sometimes kaolinite turns into chlorite or illite (Middleton 2003). Usually, clay minerals occur in assemblages and that makes the identification of a specific mineral difficult. Clay mineral groups that are the main focus in this thesis are smectites, illites, chlorites and kaolinites.

2.1 Mineralogy, structure, and properties of clays

The basic phyllosilicate structures of clay minerals are composed of tetrahedron and/or octahedron (Lewis & McConchie 1994). Combined tetrahedron form octahedra and three octahedra is the structure of the smallest structural unit of octahedral sheet. The octahedral sheet is called dioctahedral if only two of the three octahedra are occupied with trivalent ions like Al^{3+} or Fe^{3+}, and if all three of the octahedra are occupied with divalent ions like Mg^{2+} or Fe^{2+}, the sheet is called trioctahedral. There is also OH groups within the sheets. Different combinations of octahedral and tetrahedral sheets form a layer and these layers form clays. For example, kaolinite groups clays have one tetrahedral sheet and one octahedral sheet (1:1 layer) (Chamley 1989). Fig 2.1 shows the basic layer structures of kaolinite, illite, smectite and chlorite.

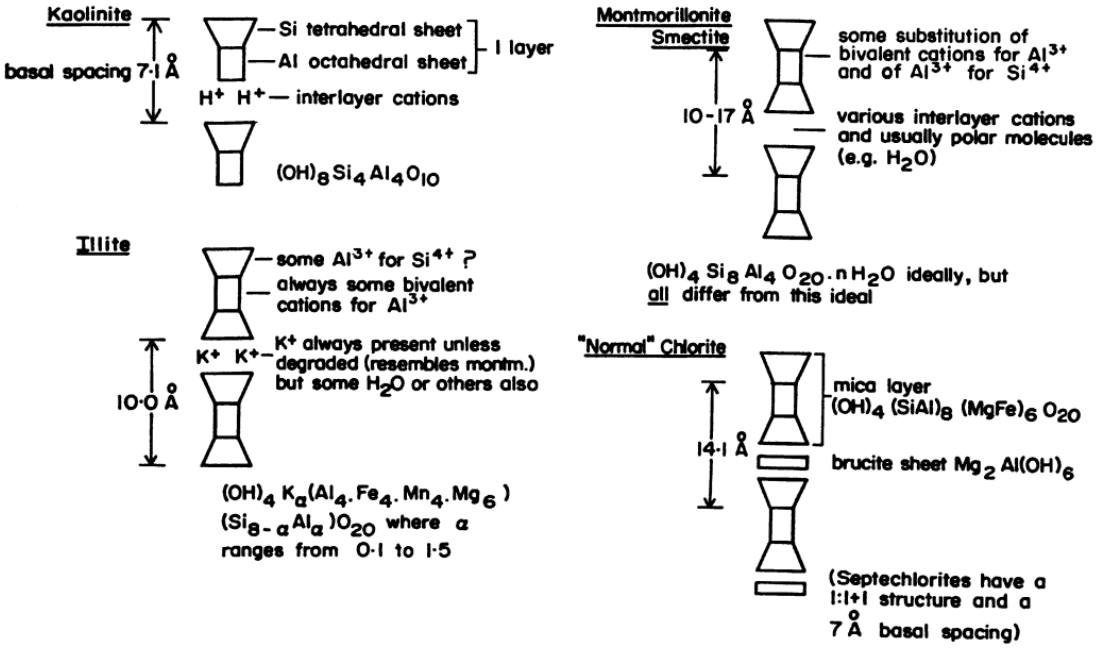

Figure 2.1 Basic structures of the four major clay groups (Lewis & McConchie 1994). Basal spacing is the property of the mineral that is used in identificationin XRD method.

The sheet like structure gives clay particles a special property; clay minerals have a large surface area compared to the volume and clay minerals are dominated by their surface. Because of the structure, clay minerals can stack up very closely and therefore the porosity of the clay is much lower than in more isometric shaped materials. Clay minerals have usually a weak charge which attracts water molecules or other ions onto outside of the particles or into the lattice (Lewis & McConchie 1994; Velde 1995). Environmentally thinking, for example smectite rich clay bedding can absorb so much water that it eventually results into a mud slide (Lewis & McConchie 1994).

Clays are silica dominated, but the occurrence of Al, Mg, Fe, K, Na and Ca elements can be used for indicators of different clay mineral types. An important identification criterion is also the difference in the distance between the crystal structures sheets, which is called the basal spacing (Velde 1992). Basal spacing is measured with Ångstöm (Å), which equals to 10^{-10} m (Meunier 2005). Different clays basal spacings differ depending on the treatment, like shown in Table 2.1.

Table 2.1 Basal spacings of the main clay groups. These changes that happen in different treatments, are used when identifying the minerals.

Clay Mineral	Basal Spacing (Å)		
	Normal condition (60°C)	Glycol ethylene treatment	Heating to 550°C
Illite	10.0 Å 5.0 Å 3.34 Å 1.99 Å	Slight shift	No change
Smectite	14.0 Å 4.5 Å	expands to 14-17 Å	No change (10 Å after heating)
Kaolinite	7.1 Å 3.58 Å	No change	Destroyed
Chlorite Mg, Fe	7.15 Å 14.1 Å 4.7 Å 3.54 Å	No change	Increase in intensity (Mg) Structure collapses (Fe)

2.2 Clay cycle

Clays are part of the geological environment. During the general geological cycle, minerals can be altered into different kinds of minerals for example due to pressure or water content changes. In the end, minerals might end up being melted into magma and the cycle starts again. The clay cycle itself begins with weathering of rock material, followed by transportation and it ends with sedimentation and burial. Clay material can change all the time according to the changes in the chemical, thermal and water content of the environment (e.g., Velde 1992). There are basically three different controllers over the clay minerals related to isotopic changes: (1) the parent minerals isotopic composition, (2) isotopic composition of the water and (3) the ratio of water/rock which affects the exchange rate of water and parent minerals (Meunier 2005). Throughout the whole cycle, the ratio of water/clay changes and it has an effect on the clay material (Lewis & McConchie 1994).

2.2.1 Weathering

Weathering is an exogenous geological process when solid rock and minerals change into a loose matter at the Earth's surface. Rock can weather either physically, chemically, or biologically. Chemical weathering gets easier when the rock is already broken physically, and plain rainwater, in other words meteoric water (Meunier 2005), is strong enough solution to dissolve ions from the rock according to Hurstinen *et al.* (1998). Chemical weathering is most common, and it can happen without any other type of weathering. There are different types of chemical weathering, but hydrolysis is the most well-known. Simplifying the process, it happens when salt and water reacts and makes an acid and a base. Hydrolysis subtracts ions out of the parent rock's minerals gradually (Chamley 1989) and it is the most common process when primary silicates are breaking down into clay minerals (Lewis & McConchie 1994).

Most of the clay materials are a result of subaerial or subaquatic weathering. High-temperature silicates weather because they become unstable at the interface where rock is exposed to air, where the environment's chemistry is different than before (cf. Velde 1992). In conclusion, weathering happens when silicates, for example olivine, are exposed to environment's temperature, precipitation, and physical erosion (Shiming *et al.* 2015). Parent rocks or minerals' different compositions can generate various types of clay minerals even when weathering in the same environment. For instance, low base rocks like granites generate mainly kaolinite and high base rocks like gabbro generate largely smectites (Birkeland 1999).

When looking at soils, in colder climates weathering is most likely physical and as the temperature and moisture rises, more chemical weathering is included into the processes and this can be seen in clay. For example, in cool-temperate areas, vermiculite is more abundant, in humid warm-temperate areas smectite is more common, and illite and chlorite are physically weathered in cold, dry environment (Chamley 1989). The way of weathering is not the only factor that determinates the end result of the clay type - time is also a factor. It makes a difference if the weathering has happened intensely and relatively fast or slowly and with care. For example, if the weathering happens in cold climate where the weathering is slow, in results that the source rocks characteristics can be evident in the clay mineralogy (Lewis & McConchie 1994). After weathering of the rock, there can also be erosion. Running water is the biggest conveyer of sediment material and clay minerals can be transported long distances as a suspension (Hurstinen *et al.* 1998).

2.2.2 Sedimentation

Clay minerals usually deposit only in very low-energy zones, in other words even the smallest current can keep the fine clay particles in suspension. But then again, if the particles have accumulated, it is very hard to erode them away (Lewis &McConchie 1994).

After sedimentation is a process called burial diagenesis, where the water/clay ratio changes again and clay becomes more dominant. The process causes the free or loosely bound water to disappear, and porosity of clay material decreases from 80 % to about 20% during the first kilometre. Burial increases the temperature by 25-30°C km^{-1} and that alters the mineral stability and different clays are made with time. During the burial unstable phases disappear so the mineralogy simplifies, and new minerals are formed (Velde 1992; Middleton 2003). For example, when depth increases enough smectite minerals could turn into illite minerals (Meunier 2005).

The type of the clay minerals can give clues about the state of source areas weathering and about sedimentation and burial. It is not always straightforward to distinguish the authigenic minerals from the detrital flakes that have been formed through continental erosion and have been transported to the site (Lewis & McConchie 1994).

2.3 Clay mineralogy groups and environmental significance and genesis

According to Velde (1992) clay minerals are usually a product of a process that happens near the surface of the earth where other silicate minerals instability produces clay. Different climates, in other words changes in temperature and precipitation, produce different kind of clay minerals. Reason for that is that weathering processes vary in arctic and tropical environments.

When thinking of the actual physical side of the clay forming, there are basically three different ways clays are formed. Rarest process is precipitation from solution, and it is very unlikely to be found. Majority of clays are formed as a result of a dissolution process where clays are the least soluble part. The third way of clays to form is to recrystallizing with temperature and pressure. Regardless of the evolving process, the most important aspect of clay formation is aqueous solution. For example, solution dissolves the building

blocks for clays from the parent mineral and from this solution clays are formed during sedimentation. The new clay material reflects the physical and chemical properties of the low-temperature aqueous environment (Velde 1992).

Also, the clay forming process can be found in weathering profiles. For example, according to Meunier (2005) weathering profiles of granitic rocks can have four different distinguished facies, starting from the bottom towards to the Earth's surface; (1) fresh rock (2) coherent weathered rock (3) saprock and (4) saprolite. Clay mineral content gets higher when going upwards from the fresh rock. Even the fresh rock facies have some kaolinite and ferriferous smectites in its crevasses. In the next facies the mineral changes happen in the contact microsystems and primary minerals affect the assemblages of clay minerals. In the third facies, saprock, illite is not any more identifiable but there are vermiculites and kaolinite. The parent rock's original structure is no longer recognisable in saprolite facies, and the clay minerals are illite+kaolinite if there is there is some K-feldspar in the surroundings. The changes happen like this mostly in temperate conditions (Meunier 2005).

Different minerals can form different clay minerals, like orthoclase can become illite (high K^+) in the right environment in granitic rocks. Plagioclase can become kaolinite and biotite into vermiculite or chlorite. Also, pyroxene can produce smectites (Velde 1992).

2.3.1 Smectite group

According to Lewis & McConchie (1994) there are different environmental factors that generally favours the formation of smectite minerals. Mixed layer smectites and illites and as well medium crystalline smectites are often formed in temperate humid climatic circumstances. Then again degraded smectites come from warm temperate and humid climates. For smectites to be formed in soils, the best condition is semi-arid climate because then evaporation is higher than precipitation. Also, high pH-conditions are needed. Smectites are formed in lakes and swamps where the water is stagnant and leaching is poor and where there is retention of Mg^{2+}, Ca^{2+}, Na^+ and silicates. The ratio of Si:Al is high, and the parent rocks are alkaline, e.g. basalts. Smectites are typically dominant in soils that have been formed in dry tropical areas and in more or less temperate, low rainfall climates, like in high planes (Velde 1992).

Clay minerals have a unique property of adsorbing water molecules onto their surfaces and some clay minerals can absorb water into their structure and therefore change volume. Smectite groups clay minerals are clays that can change their volume by attracting water, or other polar molecules like ethylene glycol, between the sheet layer of their structure. As the volume of mineral increases, the size of the basal spacing increases. This 5-7 Å increase in basal spacing affected by the ethylene glycol treatment, helps the identification of smectite minerals in XRD analyses (Velde 1992).

Typical minerals that are included in the smectite group are e.g., beidellite, montmorillonite and saponite (Velde 1995). Montmorillonite and beidellite are aluminium dioctahedral and nontrite is dioctahedral Fe-smectite. Montmorillonite clays are often created from acid tuffs and bentonite clay is a product of the weathering of volcanic ash. Nontronite is an authigenic clay and it can be formed from basalts and ultramafic rocks (Haldar & Tišljar 2014). Some trioctahedral smectites are hectorite, saponite and sauconite. The term bentonite is often used when talking about smectite minerals without taking a stand on the origin of the clay (Murray 2006).

2.3.2 Illite

Illite clays can form in temperate humid climates but also in conditions where there are moderate rainfall including wetting and drying in a cyclical manner. This kind of environment often produces podzol type soil (Velde 1992) which is typical for example in Finland. Very cold and very dry climates are environments where illites produced. Illites are quite resistant minerals and can go through a long transportation for example in glaciers (Chamley 1989). Illites can be produced both in marine and in non-marine condition and calcium carbonate is often present. The environment should be near neutral or slightly alkaline when considering pH-value. Alkaline cations especially K^+ are in retention and Si:Al ratio is high. For the source material for example feldspars and micas are ideal (Lewis & McConchie 1994). Often micaceous minerals that are clay-sized fraction in sedimentary rocks, are named illites. Chlorites can also be formed with illites in temperate humid conditions (Chamley 1989).

2.3.3 Chlorite

Chlorite is a common mineral to be transported into oceans as a weathering product. It is also common in high-latitude oceans sediments (Worden *et al.* 2020). Physical weathering in both very cold and dry environments result in abundance of chlorite and illite in rock-derived clay minerals which is due to a weak leaching. Also, desert erosion can lead to an abundance of chloritic minerals. Chlorite group minerals can be formed in marine environments where the leaching is weak, and the environment is near neutral or alkaline in pH, but they are not very resistant to transport or weathering (Chamley 1989). Chlorite clays are aluminosilicate minerals and chlorites like retention of Mg^{2+} and $Fe^{2+\text{ and }3+}$ and when considering the genetic environment, reduction of Fe^{3+} to Fe^{2+} is favourable. Parent rocks are alkaline, e.g. basalts. If chlorite is formed in sedimentary conditions, it is often transformed from smectite clays through diagenesis (Lewis & McConchie 1994).

Most of the chlorites are trioctahedral but some are dioctahedral like dombassite. Iron-rich chlorites that occur in iron-ore deposits are called chamosites, and other minerals that belong to the chlorite group are e.g., dombassite and sudoite. Clinochlore is also a common Fe-bearing chlorite group mineral (Chamley 1989).

2.3.4 Kaolinite group

Places where the leaching is at its highest, like wet tropics or under peat layers where the organic materials have flushed through the system, kaolinite formations are produced and as well are illites (Chamley 1989; Velde 1992; Lewis & McConchie 1994). Kaolinites form mainly during pedogenetic processes in surficial environments and sometimes in early diagenesis. Kaolinization is a term that can be used to refer a weathering process in Mesozoic time when climate was warm and humid (Chamley 1989). Because kaolinite needs acidic leaching conditions, it is the only clay group that cannot be formed in marine environments. This kind of leaching in soils requires higher precipitation than evaporation. When leaching happens in nonmarine conditions, Ca^{2+}, Mg^{2+}, $Fe^{2+\text{ and }3+}$, Na^{+} and K^{+} are extracted from the material. Aluminium silica ratio is high, and the parent material is acidic, like granites or rhyolites (Lewis & McConchie 1994).

It can be said that if there are large amounts of kaolinites in deposits in temperate environments, they are most likely from paleosols like regoliths and have been redeposited by glacial processes like glacial erosion. In northern hemisphere kaolinites are often from Paleozoic-Mesozoic era paleosols. Kaolinite is a very resistant mineral, and it can withstand long transportations. Other clay minerals that belong to the kaolinite group are for example dickite, nacrite as polymorphs of kaolinite and halloysite. Dickite often is connected to specific hydrothermal environments and halloysite is a hydrated kaolinite and it is a mineral that is a product of weathering (Chamley 1989).

3. GEOLOGY AND HISTORY OF LANDSORT DEEP, BALTIC SEA

3.1 Geology of Landsort Deep area

One of the world's largest intracontinental basin is the Baltic Sea Basin (BSB) and the Landsort Deep is the deepest 459 meters deep sub-basin in the Baltic Sea and it holds about 14 000 years of sediments. It is part of the Gotland basin. The BSB has four times larger drainage area than the basin itself and the drainage area has been affected by many glaciations and deglaciations, sea level changes and large shifts in sedimentation patterns (Andrén *et al.* 2015a).

The area where the Landsort Deep is situated, is geologically the Bergslagen area which consists of Palaeoproterozoic (2.5-1.6 Ga) rocks beneath the Quaternary sediment. Bergslagen area is part of the Svecofennian province. The bedrock is a product of an arc-type volcanism and simultaneous plutonism (Lahtinen 2012). The rocks are linked to Svecofennian orogeny c. 1.95-1.80 Ga (Stephens 2020), sedimentary and volcanic rocks are c. 1.95-1.80 Ga old and plutonic rocks c. 1.96-1.84 Ga old. There are also metacarbonate rocks but rocks including graphite are rare (Lahtinen 2012). There is evidence of some lateritic paleosols in the Bergslagen area and these are assumed to be c. 1.87-1.80 Ga years old (Lahtinen & Nironen 2010).

There is a possibility that at the Landsort Deep area there is Phanerozoic sedimentary rocks covering the crystalline bedrock, like in Poland and Denmark and parts of the Baltic Sea. Landsort Deep has preserved some Mesoproterozoic red-type Jotnian sandstones (Beckholmen & Tirén 2009).

Some parts of the Baltic Sea depression are contemporary with the thinning of the crust which happened when rapakivi granites were formed about 1.6 Ga years ago. There are several different structural orientations in the Baltic Sea, N-S, ENE to NE and NW, which are the most prominent structures (Beckholmen & Tirén 2009). The present-day Baltic Sea is a formation that is a combination of tectonic processes and glacial erosions, so the Landsort Deep is most likely a combination of a bedrock structure, a fault, and possible glacial erosion (Beckholmen & Tirén 2009, Harff *et al.* 2011). Most of the surrounding drainage area of the Baltic Sea is Paleozoic-Mesozoic era crystalline and metamorphic

rocks, for example granites and gneisses. On top of the bedrock there aret several till deposits as remnants of many glaciations and deglaciations. (e.g., Hurstinen *et al.* 1998; Kleman *et al.* 2008; Schoning & Wahlgren 2019)

3.2. The present and past Baltic Sea

The Baltic Sea is about 412 000 km^2 large basin area with average depth of 55 m (Harff *et al.* 2011) and currently, it is the world's largest dead zone, in other words an area that has no oxygen at the bottom of the sea. Often hypoxia is mentioned when talking about anoxic environments. It is a situation that occurs when dissolved oxygen (DO) drops under $\leq$2 ml of O_2/litre (Diaz & Rosenberg 2008). These days salinity of the Baltic Sea is approximately 7 in surface waters, lower in northern parts and higher in central areas, and about 11 to 13 in deeper parts of the basin. Due to the vertical salinity differences, there is a permanent halocline in about ~80 m deep at the Landsort Deep area and it prevents vertical mixing of the more oxygenous surface water with the hypoxic bottom water (Mohrholz *et al.* 2015).

The Baltic Sea has had many different stages in the past and the changes in environment can be seen in the stratigraphy of its marine sediments. For example, there has been changes in size of the basin, water level and salinity (Harff *et al.* 2011). Sedimentation rates have also changed through time, from ~100 cm/ky to ~650 cm/ky in the last 12 000 years (Obrochta *et al.*2017).

The Eemian Baltic Sea was before the latest ice age (Weichselian) and it had much higher sea level than the present sea has, e.g., Fennoscandia was an island because there was a pathway to the Barents Sea through Karelia (Koivisto *et al.* 2004). Water surface at western Baltic Sea Basin was about 6°C higher in temperature and salinity was about 15% higher than present but also in the eastern BSB salinity and water temperature (about 2.5 °C) at the bottom of the sea were lower. This might have created a salinity stratification which led to a hypoxic bottom condition (Harff *et al.* 2011). During this time sulphuric loams were deposited on the bottom of the sea and shallow waters (Koivisto *et al.* 2004).

About 16 000 years ago after the Eem Sea became the Baltic Ice Lake, BIL (12 600-10 300 BP) (Harff *et al.* 2011). The lake was at some point about 25 metres higher than sea level and thick varved clays were formed during this time (Koivisto *et al.* 2004). Varved

clays formed in proximal areas of the ice sheet and at the more distal areas, homogeneous clay was deposited. In the BIL, there were hardly any organic productivity or diatoms (Harff *et al.* 2011).

The water level of the BIL dropped to sea level and that was the onset of the next stage, the Yoldia Sea, YL (c. 10 300-9 500 BP). For the first 300 years there was no saline water, so varved clays were able to form. After that it had a brackish phase that had possibly a halocline because there has been evidence of some sulphide banding. At the end of the Yoldia Sea stage most of the present-day Baltic Sea area was deglaciated. (Harff *et al.* 2011) In total Yoldia Sea stage lasted about 800 years and at first it deposited varved clays, but later more homogenous clay was deposited (Koivisto *et al.* 2004).

Then was Anchylus Lake (AL) stage and this stage lasted c. 9 500-8 000 BP. Due to the last deglaciation water, the water in Anchylus had very little organic material. Water body was well oxygenated and well mixed. There is evidence of sulphide-banded sediments, but it is more likely that they are due to a H_2S diffusion from other, younger deposits than a straight evidence of anoxic conditions (Sohlenius *et al.* 2001).

After that there was a short brackish water phase, The Mastogloia Sea, in some studies called Initial Littorina Sea (Harff *et al.* 2011). The Littorina Sea was about 7500-2500 years ago but the end cannot be precisely defined because the salinity of the sea has been gradually dropping to the level it is presently. The start of the Littorina Sea shows up clearly in stratigraphy as an increase in organic matter and brackish marine diatoms (Sohlenius *et al.* 2001). The Littorina phase was the warmest phase after deglaciation and during this time some muds and sulphuric clays were deposited (Koivisto *et al.* 2004).

3.3 The Landsort Deep sediments

The Integrated Ocean Drilling Program (IODP) Expedition 347 drilled the Landsort Deep sediments at Site M0063 (Andrén *et al.* 2015b). Research drilling recorded mostly clay rich sediments of the younger geological time mostly Quaternary to present. Fig 3.1 is a graphic lithology log from the publication of Andrén (2015b) and it shows how the different stratigraphic units are correlated to the drilled core. The stratigraphy is a summary of Hole M0063D with some added information from Hole M0062A, but it can be used as a model for Hole M0063C. Stratigraphic units from I to VI are mainly clay sized minerals, for the exception of IIIA which has silt in it. Unit VII is a subglacial till deposition. Units

are divided on the interpretation that they represent different stages of the Baltic Sea, for example Unit II is thought to be Ancylus Lake sediments and Unit IV perhaps the Yoldia Sea deposits. Units I, II, III and IV have subunits, because there are changes for example in clay colour, lamination and/or sorting. These units from Andrén *et al.* (2015b) are used in this study as well due to its simplicity.

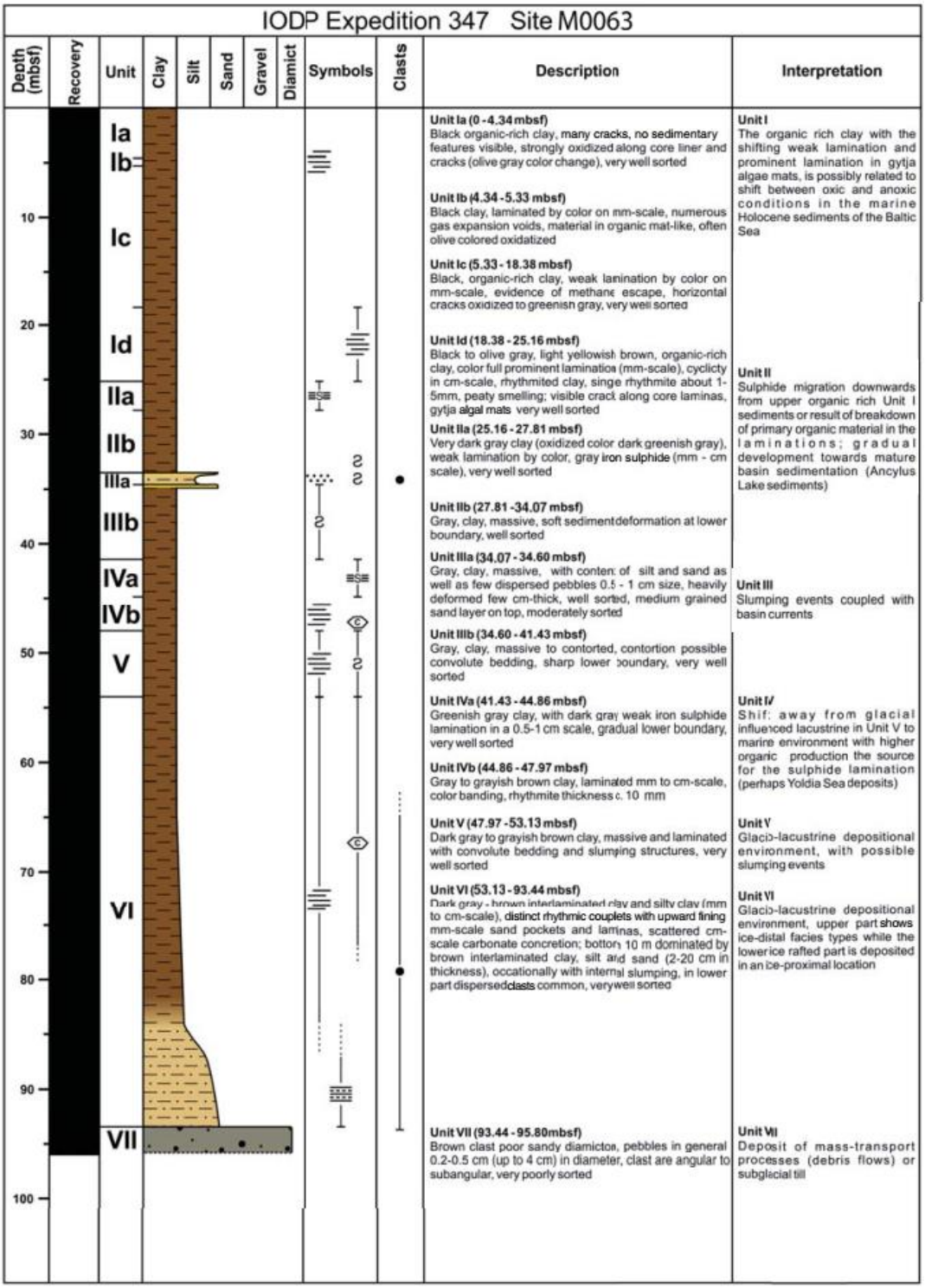

Figure 3.1 A graphic lithology log representing a summary of Hole M0063D with some added information from Hole M0063A (Andrén et al, 2015b). Even though the composite is about Hole M0063D, it can be implemented with Hole M0063C.

Unit I is a deposit that composes of organic-rich clays. Subunit IC has clays that are very well sorted, black in colour and with only weak lamination. Due to some oxidation, there is a greenish tint. The best-preserved subunit ID form Unit I is black to olive-grey, and some yellowish-brown clay and it has very clear laminations. The shifting of weak and prominent laminations could be associated with changes between oxic and anoxic conditions. Unit II clays have been associated to Ancylus Lake sediments. Organic content is lower in Unit II than in Unit I and the dividing into two subunits was due to a clear change from homogenous to laminated clays. Subunit IIA is dark grey clays with some weak millimetre to centimetre thick iron sulphide stained very dark grey laminations. Overall, the clay is very well sorted. In subunit IIB there is lamination, and the homogenous clay is grey and well sorted (Andrén *et al*. 2015b).

Unit III is divided into two subunits and both of their lower boundaries are sharp and towards upper boundary, there are sand laminae. Subunits IIIA has a heavily deformed top part which is a well sorted sand layer. Underneath that is massive, somewhat sorted grey clay that has some silt and sand. Subunit IIIB has a well sorted medium grained sand layer and a very well sorted clay layer with a sharp lower boundary. Both subunits are disturbed by the coring. This unit is a combination of two slumping events coupled to basin currents (Andrén *et al.* 2015b).

Unit IV is also divided into two subunits. Subunit IVA is grey clay with greenish tint and very well sorted with some weak iron sulphide lamination that is dark grey. Subunit IVB is also very well sorted and laminated clays, but the colour is grayish brown. The laminae are thinner than in subunit IVA. This unit is connected to Yoldia Sea stage deposits (Andrén *et al.* 2015b).

Units V and VI are both possibly glaciolacustrine depositional environment and neither of them have subunits. Unit V has very well sorted clays that are dark grey to greyish brown. There are contorted silt laminae in the internal structures. Lamination indicates glaciolacustrine environments and convolute beddings can be reworked in a slump event. Thickest unit is Unit VI, in its upper part is dark grey-brown clay interlaminated by millimetre-scale silt laminae and when going down there are several varves with sand laminae and pockets (Andrén *et al.* 2015b).

4. GENERAL METHODS TO STUDY CLAY MINERALS

Clay minerals are usually not seen with a regular microscope so there are other methods to identify or characterize them, for example thermogravimetric analysis (TGA), differential thermal analysis, infrared spectral analysis (IR) and a range of electron microscopes (Velde 1992). For the fine-grained sediments, the basic method is X-ray diffraction (XRD) (Hardy & Tucker 1988), which is the quantitative analysis method that was used in this thesis. Usually, there are many different structural clays in one sample and X-ray diffraction helps to identify these different clays (Fig 4.1) by measuring the basal spacings (Å) (Velde 1992).

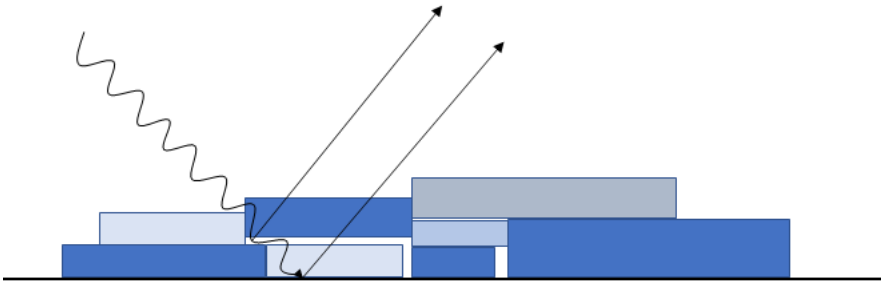

Figure 4.1 An illustration of an oriented sample. It shows how the x-rays diffract when the clays are parallel on the plate of the preparate.

4.1. Theory of X-ray diffraction

The x-rays that are used to measure basal spacings are created in a Röntgen X-ray tube with high energy electrons. Electrons are bombarded from heated filament towards a metal anode and from there the resulting radiation goes through a thin beryllium window. Depending on the sample, there are many different metals that can be used as an anode target, for example Cu, Cr, Fe, Co, Mo and Ag (Hardy & Tucker 1988). In this thesis a cobalt anode was used. Normally a copper anode is preferred in clay studies, but if the sample is thought to consist higher levels of iron minerals, a copper anode causes it to emit iron fluorescence radiation (Hardy & Tucker 1988).

The radiation that goes through the beryllium window consists of white radiation which is caused by the electrons changing their kinetic energy to X-rays and characteristic radiation that is formed according to the anodes' atom orbital electrons. With a thin metal foil

close to the beryllium window called β filter, the radiation is transformed into a monochromatic radiation. Monochromatic radiation means single wavelength so in other word some of the wavelengths have been removed from the radiation (Hardy & Tucker 1988).

A subparallel x-ray beam is produced by a divergent slit and directed towards a sample. When the x-ray beam reaches the sample in a right angle in relation to the planes of the minerals in the sample, the beam diffracts as Bragg's law (Formula 4.1) suggests (Hardy & Tucker 1988).

$$n\lambda = 2d \sin\theta \qquad \text{Formula 4.1}$$

λ = wavelength of incoming x-rays

θ = angle of diffraction

n = interger

d = lattice spacing (Å)

From the sample the diffracted x-ray goes through a receiving slit and collimator. Before the x-ray arrives to the detector, there is a scatter slit that reduces the scattered x-rays so there are only diffracted beams that are detected. The signal received by the detector is amplified and after that it is sent to the electronic recording equipment (Hardy & Tucker 1988). All this information is finally transformed into charts that can be modified and quantitatively analysed (Meunier 2005).

4.2 Other commonly used methods

X-ray diffraction is common and effective way to identify clay minerals, but there are other methods as well. Thermo-gravimetric analysis (TGA) method is used to figure out how much of absorbed, zeolite, bound or crystalline water there is in the clay material. For example, absorbed water disappears when clay mass is heated to 80-90°C and crystalline water which is bound to the structure (OH) needs 500°C or more to be released from the mineral. Infrared (IR) spectral analysis cannot really identify clay differences, so it is used to characterize clays. The method measures how much of the infrared radiation the clay structure absorbs and this shows how much energy does the OH bond in the sheet structure have. Electron microscopes, like scanning electron microscope (SEM) or

transmission electron microscope (TEM), use electron beams to form images of the studied material, for example clay minerals. SEM provides the morphology of aggregates and TEM gives the shapes and compositions of a single crystal. Cation exchange capacity (CEC) measures clay minerals surface area and its charge. This determines the clay structures amount of exchange ions (Velde 1992).

5. MATERIALS AND METHODS USED IN THIS STUDY

Out of each clay specimen it is possible to make three or four different preparations. One preparation is air-dried, another one is heated up to 550° Celsius and the third is treated with ethylene glycol. The air-dried preparation could show the four main clay minerals chlorite, illite, smectite and kaolinite. The heating destroys kaolinite and some of the chlorites and the ethylene glycol treatment swells smectite minerals, so they are more detectable (Hardy & Tucker 1988). For XRD, clay minerals are supposed to be oriented in the preparations (Velde 1992).

Sample preparations were made at the OMS (Oulu Mining School) Research Centre and the samples came from GTK (Geological Survey of Finland) in relation to IODP Expedition 347 project. After correlating the samples to the right stratigraphic levels, 17 samples were chosen. Out of each sample, three preparates were made so in total there were 51 preparates.

Everything began with first taking 3 grams of clay sediment from the sample to a plastic sampling tube with a plastic spoon. Distilled water was added until there was 20 ml of substance. Sampling tube was shaken by hand and with a mechanical shaking device until clay was dissolved into the water. At the end, 15 ml of distilled water was added so all the clay particles would be at the same solution and not at the walls or at the cap of the sampling tube. In total, there was 35 ml of solution. Then two or four sampling tubes were centrifuged for one minute at 1000 rpm (rounds per minute). Centrifuge needs to be in balance and for that reason there should be two or four tubes at the same time (Fig 5.1 e).

After one-minute centrifuging, 22.5 ml of the solution was poured into another clean plastic tube. Pouring needed to be made with care, so the bottom part of the concentrated

solution would not come to the new plastic tube. The 22.5 ml of solution was then centrifuged for 15 minutes at 1000 rpm. Purpose was to get the smallest particles, in other words clay, to concentrate at the bottom of the sampling tube. Then the suspension was poured out of the sampling tube, which meant there is only clay concentrate, and a drop of water, at the sampling tube. The excess suspension from the second sampling tube was poured into the first tube because if the preparates were somehow not viable, new preparates could be made from the same solution.

Concentrate at the bottom of the sampling tube was mixed properly with a pipette and with a pipette the clay matter was put on three glass sheets, five drops in each. Glass sheets were cleaned with alcohol beforehand. Clay matter needed to be spread a little bit with a pipette. After that, the class preparates were put in an oven in 60°C for at least two hours. Then the dry samples were placed in an exicator for safekeeping like shown in Fig 5.1 (f).

Third of the preparates were heated in an oven for two hours in 550°C and then put back to the exicator. Another third was treated with ethylene glycol. There was ethylene glycol liquid in a small exicator, and the air was removed from it after the samples were placed in the exicator. The small exicator was put in an oven for two hours at 60°C. The ethylene glycol treated samples needed to be examined with the XRD right after the treatment, in conclusion, after the samples were taken out of the exicator, they were taken to the CMA (Centre for Material Analysis) to be examined. Other samples were not in a hurry, because their treatment is stable and their XRD examination was made later.

Figure 5.1 Pictures throughout the process of making of the samples at the Oulu Mining School laboratory. (a) The clay sample bags and some distilled water that was used to disolve the solid clay into solution. (b) The mechanical vibrator that helped dissolving the clay. (c) Clay/water solution before centrifuge. (d) Preparetes in the oven drying in 60°C. (e) Sampling tubes in centrifuge. (f) Completed samples in an exicator. (g) About 3 g of clay in sampling tube. (h) How the fine material was taken from the sampling tube with a pipet.

5.1 XRD analysis

The preparates were measured at the Centre for Material Analysis at University of Oulu. Rigaku SmartLab 9kW was the XRD system that was used to study the powder clay samples. Measurements were done with Co source lamp with 45kV and 130 mA settings and Bragg-Brentano para-focusing geometry (300mm goniometer). Rigaku XRD system in Centre for Material Analysis didn't have monochromatizating option but Kb filter was used to reduce the influence on the powder pattern. Slits are 5 degrees both in sources side and analyser side. To limit the beam divergence a 0.5 degrees incident slit was used. Acquisition speed is 3 degrees per minute with step 0.02 deg/step. Limiting slit of 10 mm was used at the source side for powder samples in standard glass holders. On the analyser side of diffractometer there was an ant scattering tube what limited fluorescence.

Before each session of experiments the sample holder and other optical components are aligned using automatic procedures as available in SmartLab Guidance software suite.

Diffractometers control software was SmartLab Guidance and PDXL2 software suite with integrated access to PDF-4 2020 database was used in qualitative and quantitative and analysing. First qualitative analysing and detecting possible clay minerals and then quantitatively analysing the relative proportions of the minerals.

There were 17 clay samples and out of each sample three preparates were made, normal condition (60°C), heated sample (550°C) and ethylene glycol treated, and all the 51 samples were measured with Rigaku SmartLab 9kW and analysed with PDXL2 software. Fig 5.2 is an example of the graph that is used in quantitative analysing the samples. Normal sample measurements are the ones that are used in analysing the results. With heated sample measurements kaolinites proportions are verified and ethylene glycol treatment confirms if there are any smectite groups minerals.

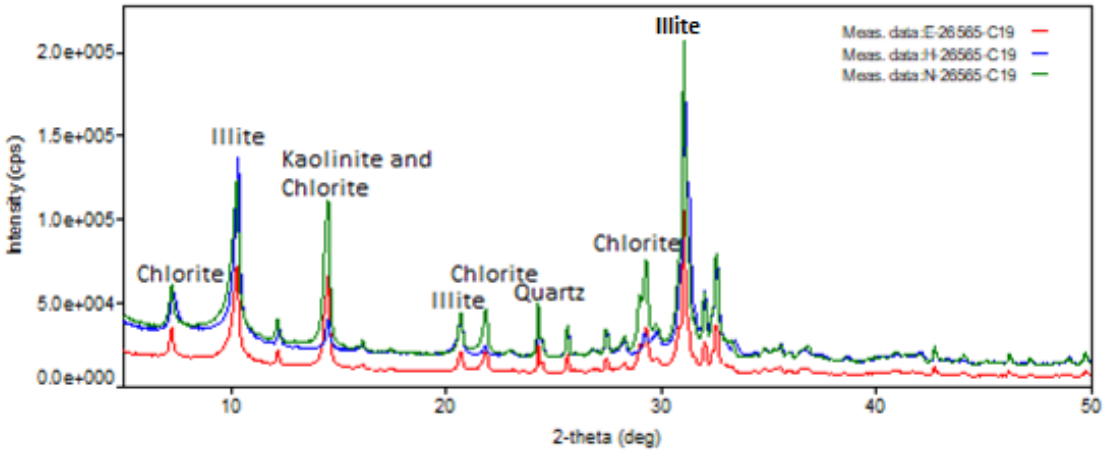

Figure 5.2 Example diffractogram of sample 26565-C19 results, that was used to identify the clay minerals. Green coloured trend is normal condition samples results, blue trend heated samples results, and red trend ethylene glycol treted samples results.

6. **RESULTS**

The idea in deciding which samples to analyse was that there would be approximately two samples out of each lithological unit. Unit IC, IIA and V have only one sample taken because they are thinner units and Units IA and IB does not have any samples, because there were none in the material given by GTK. In Table 6.1 there is all of the sample points and their correlation to the lithological unit that was interpreted from the IODP study material (Andrén *et al.* 2015b). Samples 26060-C10 and 26172-C12 were taken from Unit ID, but the preparates from 26172-C12 were too thin and XRD wasn't able to give any results. Therefore 26172-C12 won't be taken into account later or be in the tables or graphs except Table 6.1.

Table 2 A list of samples from Site M0063C and their location to lithostratigraphic units, including the depth of each clay sample (mbsf).

SAMPLE ID	LITHOLOGICAL UNIT	MBSF
26034-C9	Unit IC	16.20
26060-C10	Unit ID	19.40
26172-C12	Unit ID	23.22
26332-C14	Unit IIA	26.12
26319-C15	Unit IIB	29.10
26435-C17	Unit IIB	32.00
26612-C18	Unit IIIA	35.12
26565-C19	Unit IIIA	36.22
26684-C20	Unit IIIB	38.63
26680-C21	Unit IIIB	40.72
26689-C21	Unit IVA	42.60
26790-C22	Unit IVA	44.06
26822-C23	Unit IVB	46.52
26959-C25	Unit IVB	48.15
26963-C25	Unit V	49.63
63362.68-70	Unit VI	54.20
63361.5-7	Unit VI	81.00

Table 6.1 A list of samples from Site M0063 and their locations related to lithostratigraphic units, including the depth of each clay sample (mbsf).

Fig 6.1 is an illustration of the stratigraphic column and gives a better idea where the samples were taken regarding the depth of the deep and the lithostratigraphic units.

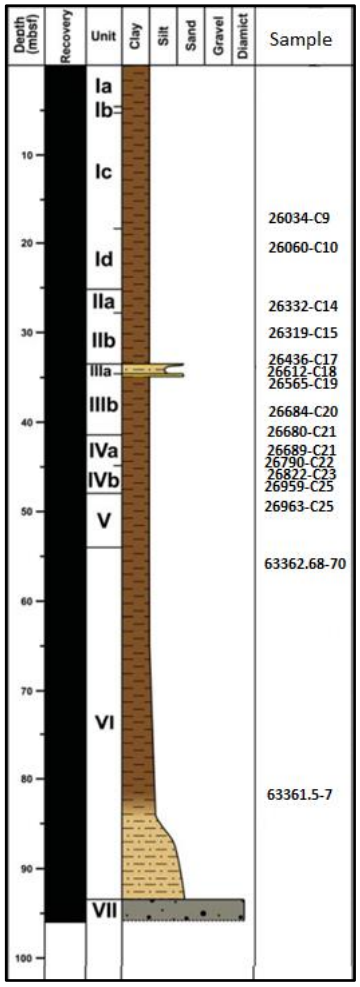

Figure 6.1 Illustration about the lithostratigraphy and where the samples were taken.

Evident clay minerals in the samples were illite, kaolinite, clinochlore as a Fe-bearing chlorite mineral and some dickite, which belongs to kaolinite group. Throughout the hole stratigraphic deposition, there was no trace of any smectite groups clay minerals. In all samples there was also some quartz and other silicate minerals like anorthite. Table 6.2 has a compilation of the results of how much there is illite, chlorite and kaolinite groups clay minerals in each sample. Table 6.2 also shows how the samples are related to stratigraphic events.

Sample 26632-C14 has relatively largest amount of illite groups minerals, 89.47% (Table 6.2). Largest percentage of chlorite minerals is in sample 63361.5-7, 56.84% and largest percentage of kaolinite minerals is in sample 26822-C23, 55.32%. The lowest portion of illite minerals is in sample 26822-C23, 21.28% chlorite minerals in sample 26332-C14,

1.44% and kaolinite minerals in 26565-C19, 6.10%. In seven samples illite minerals are the dominant part with percentages over 50%. In six samples kaolinite minerals are the smallest proportion and the percentages are under 20% and in seven samples chlorite mineral content is between 14-28%. Standard deviation for illite groups minerals is about 17%, for chlorite and kaolinite group ~15%.

There are some differences in the mineral assemblages when looking at the different lithological units. The differences are more visible in graph form (Fig 6.2) than in table form. Unit I has from 27% to 39% of illites, 54% to 41% chlorites and ~18% kaolinites. Unit II has a peak of illites (89%) at the shallowest sample point and then it goes back to 33% and 46%. Chlorite has the lowest percentage (1.44%) in Unit II and the other values are c. 15%. Kaolinites have a clear increase from 9% up to 51%. After that there is Unit III which has fluctuating values between illites and chlorites. Illite values are high, fluctuating between 35% and 65% and chlorites fluctuate between 27% and 35%. Kaolinite stays low between 6% and 14%, except sample 26612-C18 which has higher amount of kaolinite (37%). Sample 26612-C18 is the shallowest sample of Unit III.

In the Unit IV the fluctuation continues but illite values are between 21% to 60%, chlorites alternate between 6% and 26%, and kaolinites change between 26% and 55%. When illite has higher values, kaolinite has lower and vice versa. Unit V has an increase in illites, or rather it comes back to normal, 56%. Chlorites are 31% and kaolinites 12%. In Unit VI illite minerals have a distinct decrease when going downwards in depth, from 42% to 24%. Chlorite minerals increase steadily from 41% to 56% and kaolinite minerals stay around the same, at ~15-18%. In three of the deepest sample points (Units V and VI) illite minerals percentage declines (56.46% to 24.87%) and chlorites increase from 31.18% to 56.84% when going deeper. From c. 26 meters to 32 meters, illite minerals proportion decline (89.47% to 33.63%) and kaolinite minerals proportion increases (9.09% to 51.06%), chlorite minerals amount remaining about the same (~14%).

Table 6.2 Compilation table about clay minerals percentages in each sample. There is illite, chlorite and kaolinite groups clay minerals and the relation of kaolinite/chlorite clays. Samples are from different stratigraphic units and subunits, and they are related to different deposits like the Baltic Ice Lake or Yoldia Sea.

Sample	Unit	MBSF	Illite group (%)	Chlorite group(%)	Kaolinite group (%)	Kaolinite/ Chlorite	Possible relations to stratigraphic events
26034-C9	I C	16.20	27.90	54.33	17.77	0.33	I: Possible shift between oxic and anoxic conditions in the marine Holocene sediments of the Baltic Sea.
26060-C10	I D	19.40	39.50	41.18	19.33	0.47	
26332-C14	II A	26.12	89.47	1.44	9.09	6.30	II: Anchylus Lake sediments.
26319-C15	II B	29.10	46.14	14.43	39.43	2.73	
26435-C17	II B	32.00	33.63	15.32	51.06	3.33	
26612-C18	III A	35.12	34.58	27.94	37.48	1.34	III: Slumping events coupled with basin currents.
26565-C19	III A	36.22	65.08	28.81	6.10	0.21	
26684-C20	III B	38.63	51.28	34.26	14.47	0.42	
26680-C21	III B	40.72	64.39	23.41	12.20	0.52	
26689-C21	IV A	42.60	34.56	25.92	39.52	1.52	IV: Perhaps Yoldia Sea deposits. Shift away from glacial influenced lacustrine to marine enviroment with higher organic production.
26790-C22	IV A	44.06	60.36	13.48	26.16	1.94	
26822-C23	IV B	46.52	21.28	23.40	55.32	2.36	
26959-C25	IV B	48.15	53.19	5.78	41.03	7.11	
26963-C25	V	49.63	56.46	31.18	12.36	0.40	V: Glacio-lacustrine depositional environment, with possible slumping events.
633962.68-70	VI	54.20	42.93	41.85	15.22	0.36	VI: Glacio-lacustrine depositional environment.
63361.5-7	VI	81.00	24.87	56.84	18.29	0.32	

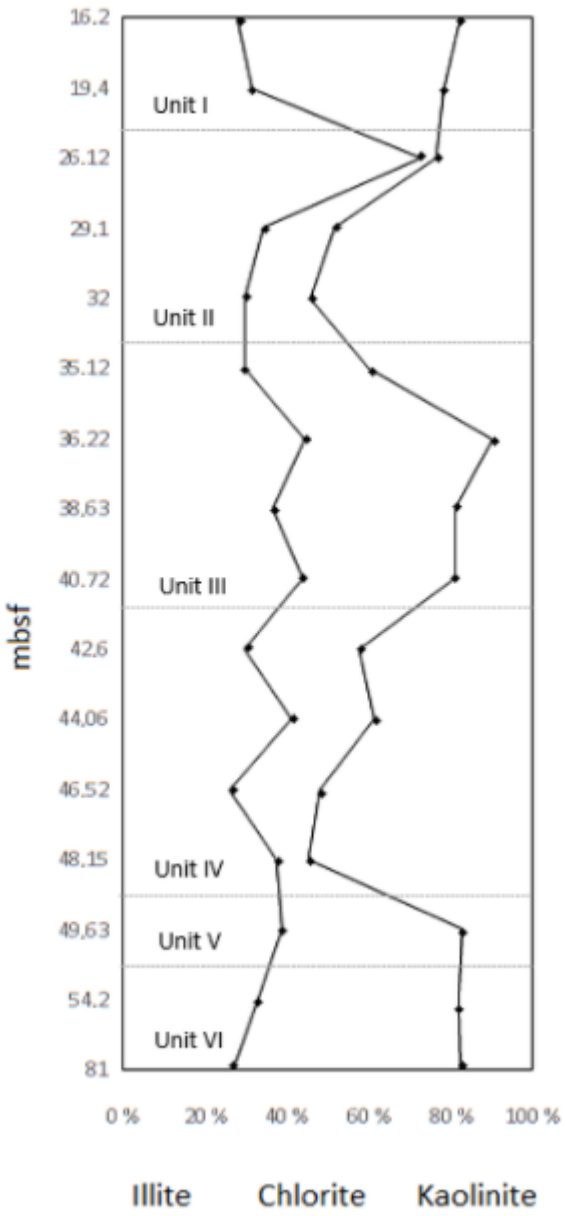

Figure 6.2 A graph of the percentages of illite, chlorite and kaolinite clay minerals in samples and their correlation to stratigraphic units.

In Table 6.2 there is the ratio of kaolinite/chlorite and in Fig 6.3 has a graph illustrating the variation of ratio. In Unit I kaolinite/chlorite ratios are 0.33 and 0.47, in Unit II rations are 6.3, 2.73 and 3.33. In Unit III the ratios are again under one for the exception of 1.34 which is in subunit IIIA. Other ratios are 0.21, 0.42 and 0.52. Unit IV has ratios of 1.52, 1.94, 2.36 and 7.10 which is clearly higher than others. Then again Unit V and VI have kaolinite/chlorite ratios under one, 0.40, 0.36 and 0.32. In other words, Units I, III, V and VI have more chlorite than kaolinite and Units II and IV have more kaolinite than chlorite. When looking at the subunits, the change of kaolinite/chlorite ratio is not noticeable, the bigger difference is between units. If the ratio number was one, it would mean that there

is the exact same amount of kaolinite and chlorite. Every time there is a transition to the other unit, the kaolinite/chlorite ratio has a slight shift towards the upcoming unit, for example when Unit III changes to Unit II, the ratio is 0.21, then 1.34 and then unit changes and the ratio is 3.33.

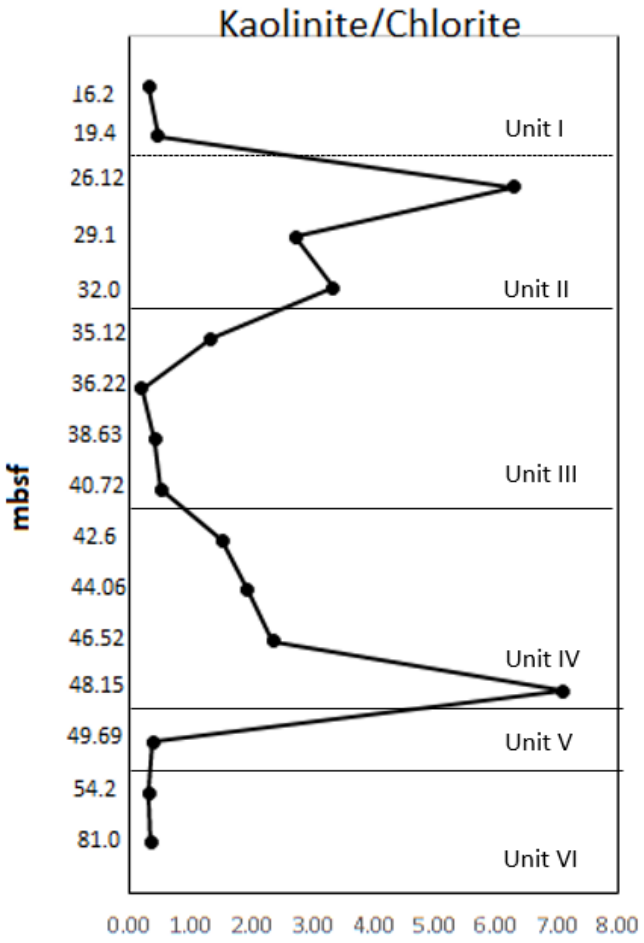

Figure 6.3 A graph about the kaolinite/chlorite ratio and how it changes through the drilling core.

According to Andrén *et al.* (2015b), Unit I sediments are marine Holocene sediments of the Baltic Sea and possibly a result of a shift from oxic to anoxic conditions (Table 6.2) Unit II sediments are from Anchylus Lake deposits and Unit III is deformed sediments that are a result of slumping events and basin currents. Unit IV deposits are assumed to deposit during Yoldia Sea events. Units V and VI are from glacio-lacustrine depositional environments, most likely from the Baltic Ice Lake period.

7. DISCUSSION

Several articles discuss about clay minerals, studying them with XRD and their meaning in sediments (e.g., Gingele & Leipe 1997; Ruikka & Strand 2002; Tankersley & Balantyne 2010; Emel'yanov & Luksha 2014). According to Emel'yanov & Luksha (2014) that there is not that much variation in clay assemblages in the resent Holocene Baltic Sea sediments. There is only illite, chlorite and kaolinite groups minerals that are being studied due to the fact that there was no smectite groups clays. This is common in other studies as well, except there can be small amounts of smectite in some deposits (Emel'yanov & Luksha 2014) Andrén *et al.* (2015) did ^{14}C dating of the first 24.6 mbsf which age was 5850 ± 120 cal yr BP.

High illite content or rapid increase of it can be associated to melting of ice sheet or that the deglaciation is happening closer to the continent. Increase of kaolinite content can be an indicator of increased glacier weathering because of the fact that kaolinite can't be formed in higher latitudes due to colder climate, therefore kaolinites found in Holocene deposits in the Baltic Sea region are from older paleosols, regoliths. If combined with decrease of illite content, it can be a proof of some kind of glacial erosion. In polar areas kaolinite comes from old sedimentary rocks perhaps from Mesozoic era and there is a plenty of Mesozoic era granitic rocks for example in south-eastern Sweden (e.g., Nysten & Jönberger 2019).

Chlorite is not very resistant to transportation, so chlorite minerals could come from closer areas or transported as ice raft debris. According to Gingele & Leike (1997) kaolinite/chlorite values typically vary between 0.5-0.6 and if the ratio is 0.8 it is possibly due to the destruction of chlorite. For example, in sample 26435-C17 the ratio is 3.33 which means that there is over three times more kaolinite compared to chlorite. Is this typical or are the high values somehow false? Also, according to Gingele & Leike (1997), if the kaolinite/chlorite ratio is high, it would need an additional input of kaolinite to the basin, in their case likely from the North Sea. The Landsort Deep is closer to Scandinavian continent than the drilling points of Gingele & Leike (1997), so it is more likely that the kaolinite comes from Swedish mainland. If, and reasonably it does, kaolinite comes from mainland Sweden and it comes through rivers, why there is no smectite if smectite often comes when there is river flow? This supports the theory that the provenance area where lay material comes from does not have smectite minerals.

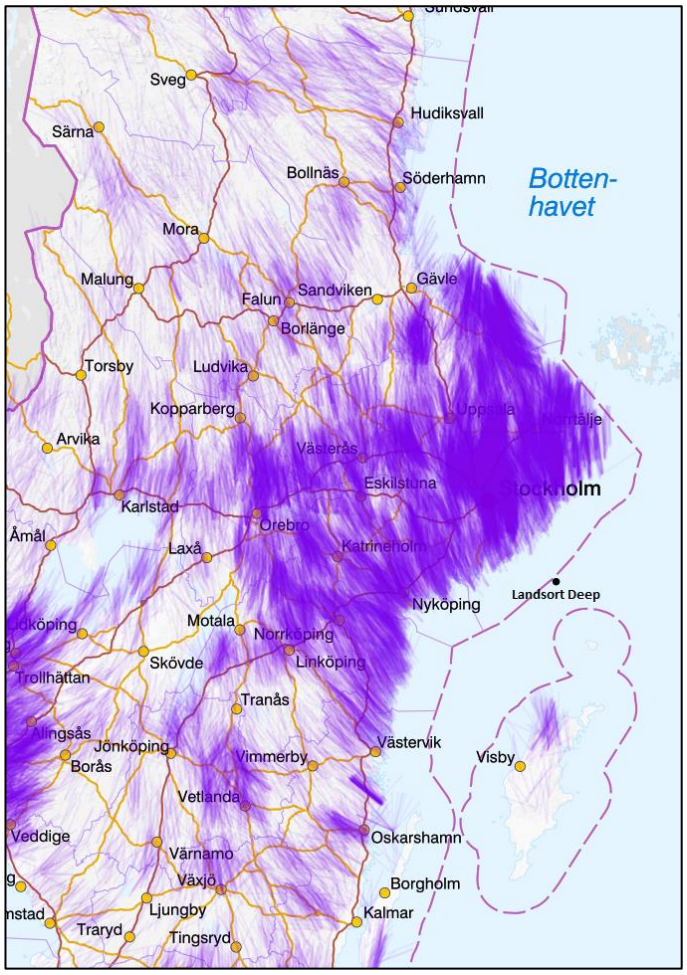

Figure 7.1 The purple lines are lineation markings that are left behind from the glaciers flow, leaving a definition of glacier lobes (© Geological Survey of Sweden).

As it shows in Fig 7.1 the lineations left behind from glacier flows are more intense than other parts of Sweden. This could indicate that the material input of ice, debris or clay is larger than in other parts of basin. Therefore, it would not be a large leap to assume that there is a possibility that the kaolinite at Landsort Deep comes mainly from mainland Sweden and not from the North Sea. Of course, it has to be taken into account that this eastern part of Sweden could better mapped then rest of Sweden. In the article of Gingele & Leipe (1997) there is some kaolinite/chlorite ratios clearly over 1, and these come from area that is in a river basin that is mostly lacustrine water (Szczecin Lagoon). The kaolinite/chlorite ratios ~1 are from basin like Bornholm, Gotland, which is in open water.

Gingele & Leipe (1997) also mentioned that kaolinite/chlorite ratio under 0.8 is characteristic to Ancylus and Yoldia surface sediments. It is also typical to dynamic areas, where Holocene sediments remix with older sediments, which can be the reason in Unit III.

Each unit of the lithostratigraphy, or a stage of the Baltic Sea, will be discussed separately. Smectite clays will be in on its own chapter because there was no trace of smectites in the samples.

7.1 Units V and VI

Units V and VI are thought to be sediments from glacio-lacustrine environments. When going towards older deposits, decreasing illite percentages support this theory. It could be thought the other way around, illite percentages increase when going from deeper sediments to higher and towards the end of the Baltic Ice Lake phase. Increasing illite is associated to melting of ice sheet. When going from newer to older sediments (49.63-81 mbsf), kaolinite values are increasing slightly from 12% to 18% and the reason for it is the fact that there is more glacier erosion. During the BIL there was no pathway to the North Sea and therefore no pulses of fresh seawater with extra kaolinite. More distinct increase of chlorite minerals (from 31% to 56%) supports this, because chlorite can come as an ice rafted debris or from short distance transportation since chlorite does not resist erosion well. Environment is getting cooler, and glaciers are advancing.

Low kaolinite/chlorite ratio (~0.36) supports the glacier erosion theory. Kaolinite/chlorite ratio decreases slowly when going downwards so could this suggest that the environment is transitioning towards closer the ice sheet, because of the high chlorite content? There is a Unit VII underneath the clay deposits that has been identified as diamicton that could be subglacial till (Andrén *et al.*2015b). As said in the study of Andrén *et al.* (2015b) Unit V has laminated clays that are an indication of possible glaciolacustrine environment and Unit VI has rhythmically banded clays that suggest they are lake deposits and in this case, glaciolacustrine deposits.

7.2 Unit IV

Lowest sample of Unit IV (26959-C25) has the highest kaolinite/chlorite ratio of 7.1, and it could be an evidence of a sudden change from lacustrine to brackish or marine environment. It is also possible that chlorite clays were destroyed in this deposit but most likely it is due to the change of salinity. This unit has two subunits A and B. Subunit IVB

has higher kaolinite/chlorite ratios (over 2.3 and 7.1), but subunit A ratios are under 2. It could be that in the start of the Yoldia Sea stage there is a pulse of fresh seawater from the North Sea and excess kaolinite comes from it and is included to the kaolinite material that is coming from continent. After the initial pulse, influence of the North Seas kaolinites gradually diminishes and the kaolinite input from rivers stay the same, but because the chlorite material that comes from the continent also stays the same, the kaolinite/chlorite ratio decreases. According to Gingele & Leipe (1997) the presence of the Yoldia Sea could be indicated by saline ingression which shows as a maximum kaolinite/chlorite ratio.

Illite percentages have higher values in each subunits lower part, and it decreases towards the surface. Subunit IVB has 53% illites in the lower sample and the other is 21% and subunit IVA has 60% illites in the lower and 34% in the higher sample. Could these increases and decreases be due to intense melting of ice sheet nearer the continent or a change in the saline content? Illite minerals major source could be Scandinavian mainland. Theory is the lower samples of subunits are the result of a deglaciation period when the ice sheet is melting at the mainland and there is more illite minerals. But the other samples from subunits are from a short period when there was more glaciation and glacier erosion that produced more kaolinite minerals alongside with it more chlorite minerals was transported to the sedimentation basin. During the Yoldia Sea stage there is still ice covering middle and northern Sweden. In the study of Obrochta *et al.* (2017) the stratigraphic sediments were dated to ~42 ambsf and it is the brackish stage of the Yoldia Sea stage, ~11 200 y BP. Last sample to be included to that is 26689-C21, the last sample of subunit IVA.

In the study of Andrén *et al.* (2015b) Unit VI is a laminated clay unit that from greyish brown lamination (subunit IVB) to lamination that is greenish grey with dark grey to black iron sulfide-stained (subunit IVA). This change from subunit IVB to subunit IVA could be a sign of sedimentary environment shifting away from glacial influenced lacustrine varvic sedimentation (Andrén *et al.* 2015b).

7.3 Unit III

Kaolinite/chlorite ratio decreases gradually in Unit III from 0.52 to 0.21 and the top sample (26612-C18) ratio is 1.34, which is significantly higher than the others. These low

ratios are characteristic to marginal areas that are dynamic and when older sediments mix up with Holocene sediments. This coincides with Andrén *et al.* (2015b) suggesting that Unit III is result of slumping events and increased near bottom hydrodynamic activity. Unit III has as well two subunits, IIIA and IIIB. Illite values are a bit higher in subunit IIIB and in subunit IIIA sample 26565-C19, but not in the top part sample. The three samples are most likely from the slumping events, but the fourth could be really part of another unit. According to Andrén *et al.* (2015b) both of subunits have sharp lower boundary and evidence of deformation in upwards section. These gradual redepositions are characteristic in slumping events and/or turbiditic events. Clay mineral stratifications are disturbed during these events.

Sample 26612-C18 could really be already from the Ancylus Lake phase. Reason behind this theory is that it has suddenly clearly higher kaolinite/chlorite ratio and illite values (~33%) are roughly the same as in subunit IIB lowest sample, 26435-C17.

7.4 Unit II

According to Andrén *et al.* (2015b) Unit II deposited during Ancylus Lake period and unit consists of two subunits, IIA and IIB. During Ancylus Lake period there was only some glacier left in the northern parts of Sweden and Norway. In western parts of the Baltic Sea the Ancylus Lake sediments have under 0.75 kaolinite/chlorite ratio (Emel'yanov & Luksha 2014) but in this study the ratio in presumed Ancylus Lake sediments is clearly over 2. In subunit IIB the ratios are 3.33 at lower sample and in higher sample it is 2.73. In the only sample from subunit IIA the ratio is 6.3. As was said in previous chapter, there is a high probability that sample 26612-C18 from subunit IIIA is also part of Unit II and possibly subunit IIB.

Because Ancylus is a lake there is no pathway to the North Sea and therefore every sediment in the basin has come from the Scandinavian mainland. Kaolinite and illite minerals are more resilient than chlorite minerals and that explains why both kaolinite and illite has high values. Due to long transportation most chlorite minerals are destroyed before they reach the Landsort Deep basin.

Why does sample 26332-C14 in subunit IIA have so much higher kaolinite/chlorite ratio and why illite percentage (89%) is so high as well? Kaolinite/chlorite ratio is high partly

because illite percentage is so high and for that reason the relative quantity of chlorite and kaolinite are so low. But the reason why illite percentage is so high is still a mystery. It would mean that somewhere close to the basin was an illite deposit that eroded to the basin, but then there would be most likely more chlorite. If illite had come from rivers, there would have been more kaolinite. It is a fair assumption that the sample 26332-C14 was made poorly and because of that the results are not that reliable. It would have made more sense if illite content had decreased gradually towards the surface and that kaolinite/chlorite ratio would do the same. After all, Ancylus Lake gradually changes to the Littorina phase without any major occurrences.

Of course, there is a possibility that sample 26332-C14 is Mastogloia phase. In brackish waters illite minerals amount increases and kaolinite/chlorite ratios decreases (Gingele & Leipe 1997). In the study of Andrén et al. (2015b) subunit IIA has weak very dark grey lamination but in subunit IIB there is no lamination, and the clays are well sorted and homogenously grey. Could it be that the weakly laminated subunit IIA is from Mastogloia phase and because of the change to brackish water from lacustrine it increased illite minerals percentages significantly? Anhylus Lake phase ended because the sea level had risen so much that it would make a new pathway to the Baltic Sea Basin. It is possible that through this pathway came more illite minerals and some kaolinite minerals which increased the kaolinite/chlorite ratio to 6.3.

7.5 Unit I

According to earlier studies (Andrén *et al.* 2015b) Unit I is most likely from early Littorina phase and not from the Ancylus Lake sediments. Kaolinite/chlorite ratios are both under 0.47, but in the study of Emel'yanov & Luksha (2014) kaolinite/chlorite ratio exceeds 0.75 in the Littorina muds in the Western Baltic Sea which is higher than in Ancylus sediments but in Bornholm Deep the kaolinite/chlorite ratio in the Littorina muds is lower than in the Ancylus sediments. Bornholm Deep is situated south from Landsort Deep. In the study of Gingele & Leipe (1997) the Littorina muds diagnostic features of kaolinite/chlorite ratios are between 0.9-1.

In Unit I Illite percentages decreases upwards, chlorite increases and kaolinite decreases. Could the decrease of illite and kaolinite mean that rivers from Scandinavian mainland

are not the primary pathways that accumulate material to the Landsort Deep. Could it be that that chlorite minerals comes somewhere closer?

The total organic carbon (TOC) had peaks in 5 mbsf (¨~7wt%) and in 20 mbsf (~9 wt%) and rest of the sediment column didn't really have any TOC, values under ~0,5 wt%. In other words, Unit I is the only unit that has significant amount of TOC. Total sulfur (TS) content had peaks as well in 5 and 20 mbsf and under 27 mbsf TS was under 0,1 wt%. This reflects the transition from freshwater to marine environment which shows as an increase of sulfate content (Andrén *et al.* 2015b).

7.6 Lack of smectite in the Baltic Sea sediments

In other publications, like in Junttila *et al*. (2010), the increase of smectite minerals is linked to the Atlantic currents strengthening in Barents Sea and in Ruikka & Strand (2001) smectite is assumed to have transported longer distances during interglacial open water periods. Smectite is often a sign of a warmer period and excess of water or a sign of a river discharge. Samples of this study are from the Yoldia Sea stage (11 600 – 10 700 BP) and Anchylus Lake stage (10 700 – 9 800 BP) apart from the three oldest ones which are possibly from BIL.

Even though it is warmer, and glacier is receding, the transportation distance of clay material doesn't necessarily lengthen because the sedimentation material consists of the same material and there is no input of smectite what could come from further. Colder polar climate is favourable in producing illite and chlorite so it might be resonable to consider that the climate just isn't suitable for smecite production. There is some basaltic and volcanic rhyolite in south-east area of Sweden (e.g., Nysten & Jönberger 2019) and these kinds of rocks can form smectite minerals in arid high planes and tropical dry climate (Velde 1992).

There are some evidence of smectite minerals at southern Sweden (e.g. Ahlberg et al. 2003) and western Sweden (Inoue *et al.* 1990). There is also evidence of smectite minerals in Bornholm Denmark (Tan et al. 2017), but not in the Landsort Deep. Due to the lack of smectite minerals it can be said that the area, where from the glacier rivers and deglaciation waters transported the clay debris to the Landsort Deep, does not have smectite minerals or they have been transformed during the transportation. And this theory can be

supported by the fact that most likely kaolinite material in basin sediments comes from river streams from continent and if smectites increase usually is due to increase of water flow, it could be interpreted that there is no smectite minerals in the provenance area.

7.7 Hypoxia, Anoxic basin

According to Zillén *et al.* (2008) hypoxia has been almost continuously present in Landsort Deep for the last c. 8500 years. There is evidence of widespread hypoxia during the Holocene Thermal Maximum (HTM), that was about 8000-4000 BP, and during the Medieval Climate Anomaly (MCA) about 1400-700 BP. Neither of these events show in this studys' sedimentary record, but there are other studies that have been made from the Site M0063, like the one done by Papadomanolaki *et al*. (2018). All of the clay minerals that have been found on the site are detrital minerals and if there was authigenic minerals, they would most likely have some kind of evidence of anoxic of oxic environment.

One good indication about the anoxic state of Landsort Deep is that the sediment record from the basin that IODP 347 Expedition was able to drill is relatively undisturbed. Some of the sediments were well laminated and there was no bioturbation below 17.6 mbsf, below the first subunit IC (Andrén *et al.* 2015b), sample 26034-C9. This would indicate that there is some oxygen at the sea bottom during this time, about 4000 years ago (Obrochta *et al.* 2017). This finding is also supported by other studies like Vallius & Kunzendorf (2001). In their study Littorina phase sediments are continuously laminated and there is no disturbance by bioturbation in the Gotland Basins sediments. And, according to Andrén *et al.* (2015c) 28m of the upper sediments are laminated, organic-rich mud that indicates that the Landsort Deep has been anoxic for the last 7000 years.

7.8 Other thoughts

Is clay mineralogy a good way to study resent Holocene ages? For example, in longer timespans the clear changes of proportions of from smectite-dominated clays to illite- and chlorite-rich clay in Oligocene was a good indication of transitioning from warmer climate to a cooler climate (possible start of glaciation) (Ehrmann *et al.* 1992).When comparing Holocene, Last Glacial Maximum (LGM), and the last glaciation in general, clay

content variations have been more stable in Holocene so the variations between clay minerals are small and need more precise studying and more data to study.

In future studies more frequent sampling would give a bit more information and it might give away the more nuanced variations in the stratigraphy. Also, some studies with microscope and grain size analysis would give more information and perhaps it would help in discovering and understanding changes between stages of the Baltic Sea. Maybe these would give a little bit more information and could have help with more precise assumptions. Or did we have enough samples that we could really make conclusions about climate or hypoxic conditions with this amount of data or are these just some sophisticated assumptions.

Could it be that the stratigraphy done by Andrén *et al.* (2015b) is somewhat distorted, could it be that really samples 26172-C12 and 26332-C14 are actually from IIIA because they looked that they had less fine material then the others. Maybe these samples have possibly more sand and other bigger grain sizes and therefore would be more likely from slumping events than? It would mean that there would be about 15-20 m of mismatching.

8. CONCLUSION

The Landsort Deep is a subbasin that accumulates terrigenous material and because the bottom of the basin has been relatively peaceful during Holocene, the collected sediment record is a good uninterrupted representation of surroundings of the Baltic Sea during Holocene. It is no wonder that there is plenty of studies done around the Baltic Sea, it is quite important waterway to many countries. Many of the studies coincided with each other about hypoxia of the Baltic Sea Basins. For the last 7000 years the deepest parts of the Baltic Sea have been anoxic, and it shows as undisturbed laminations in Holocene sediments. In the Landsort Deep drillings only in the top part sediments were some evidences of bioturbation which is a sign of oxygen in sediment water interface.

Some of my study results coincide with previews studies like that the Units V and VI are most likely from the Baltic Ice Lake phase and that some of the kaolinite clays come from the North Sea like in Unit IV. Unit IV has suddenly higher kaolinite than in Unit V and that is explainable due to the fact that when the Baltic Ice Lake transitioned to the Yoldia Sea, there was a pulse of fresh seawater from the North Sea and that water had more kaolinite.

In every deposit there could be more explanations than just one for the clay material that has deposited. Both Ancylus Lake and Yoldia Sea have high kaolinite/chlorite ratios, even though they are completely different stages of the Baltic Sea. Yoldia Sea had high kaolinite/chlorite ratio because there were two inputs of kaolinite to the basin at that time, the North Sea and the glacier. Ancylus Lake had high kaolinite/chlorite ratio most likely because chlorite minerals were destroyed possibly during the long transportation. And the reason why the Baltic Ice Lake had low kaolinite/chlorite ratios? Chlorite minerals came from ice rafted debris (IRD) and ice sheet melting was minor and further away from continent so there was not that much of illite minerals or kaolinite minerals, compared to chlorites.

Some of the study results do not necessarily coincide with previews studies like sample 26435-C17. Because of the clay contents, it would be more reasonable that it was part of Unit II then Unit III. There is also a reason to believe that sample 26332-C14 is not totally reliable, because the results from XRD-analysis were so radically different than the other results from other samples. It would be more understandable that the illite value is lower

and kaolinite/chlorite ratio as well so it would be a gradual transition from Ancylus Lake to Littorina.

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